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Experimental modeling of methane release from intrapermafrost relic gas hydrates when sediment temperature change

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ABSTRACT

Special experiment on metastable relic methane hydrates behavior in clay-enriched sediment recovered from "Yamal ice crater" has been arranged to check sensitivity of relic gas hydrates to small temperature changes in permafrost section. The experiment was conducted in an experimental cell with P/T conditions registration and equipped by stirrer. Prepared sample was saturated by methane hydrates and chilled to temperature −7 °C, and then cell was depressurized to form metastable hydrates. After few times of depressurization (extra pressure relief) and pressure stabilization for a relatively long time at temperature −6.79 °C, the sample was slowly heated to temperature +2.0 °C. It was established, that even small temperature changes have a great impact to metastable intrapermafrost hydrates. The majority of remaining (after depressurization) metastable hydrates had decomposed in the temperature range −6.75–−6.57 °C practically immediately after the sample slow heating beginning, confirming the supposition, that permafrost can produce huge volumes of greenhouse gases even at small surface (climatic) changes without sediment ice complete thawing.

1. Introduction

Intensive development of oil and gas fields in permafrost regions is accomplished by observations of gas liberations from the ground around production wells and in neighboring areas. From the first time the reason of these liberations was assumed as hydrocarbon gas leakage from upper production horizons along well columns. But special studies of the gas gave another reason.

Weak and/or sudden gas liberations from permafrost are known for a while onshore and offshore (Yakushev, 2009; Anthony et al., 2010; Shakhova et al., 2010). Usually they are explained by microbial (marsh) gas release from subsurface (depth first meters) thawing sediments (Anthony et al., 2010; Walter et al., 2008; Rivkina et al., 1998) or local breakthrough through permafrost section of deep thermogenic gas (Kuzin, 1992). But long-time field and laboratory research of permafrost drill cores, recovered at the north of West Siberia from different depth have shown, that (Yakushev, 2009):

- Permafrost section is not impermeable for gas completely and can hold intrapermafrost gas accumulations,
- Gas along permafrost section has local, microbial genesis (result of buried organic matter microbial processing) presumably and only sometimes is mixed with more deep, thermogenic gas,
- Considerable part of intrapermafrost gas is concentrated in the form of metastable hydrates.

The most unusual thing when frozen drill cores studies was discovery of metastable gas hydrates at depths from first meters to 250 m, existing there due to gas hydrate self-preservation phenomenon (Yakushev, 1989). Their presence was confirmed by drill cores studies in the north of West Siberia (Istomin and Yakushev, 1992) and north of Canada (Dallimore and Collett, 1995). They can exist only in ice-containing permafrost sediments, because ice prevents them from decomposition. They have been formed in ancient time, when favorable for hydrate formation thermodynamic conditions existed in the section and are safe by now due to their partial decomposition at subzero temperatures accomplished by isolating ice film formation on their surface. So they were named "relic" hydrates (Yakushev, 1989). And these relic hydrates contain huge volumes of intrapermafrost methane (1 m^3 of gas hydrate contain more than 160 m^3 of gas at standard conditions). Their stability and sensitivity to different impacts in permafrost is a great question.

Intrapermafrost relic hydrates can occur in frozen sands as well in loams, silks and clays. Hydrate-containing sands with metastable hydrates are modeling experimentally well enough due to good permeability of sands (see for example Wright et al., 1999; Chuvilin and

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Grebenkin, 2015). However experimental modeling of hydrate-saturated clay-enriched samples is a hard task due to low permeability of clays for gas. Nevertheless the majority of gas hydrate resources is attributed to marine clay deposits (Boswell and Collett, 2006). This means, that gas hydrates can also occur in continental clay deposits in areas of permafrost spreading. Moreover they were encountered in frozen clay-enriched drill cores in metastable (relic) state in Yamal peninsula (north of West Siberia) at shallow permafrost depth (less than 200 m) (Yakushev, 2009). These relic gas hydrates represent the most sensible part of all natural gas hydrate resources in the Earth when climate change. Metastable hydrates sensitivity to temperature changes in clay-enriched frozen sediments is not known due to difficulties with drill cores recovery and storage and with experimental production of synthetic samples. This paper discusses an attempt of experimental production of hydrate-containing sample using natural clay taken from the inner side of "Yamal ice crater" and hydrate behavior when slow heating at subzero temperatures.

2. Yamal "ice crater"

In July 2014, great attention of the Russian scientific community was focused on the information on a giant deep funnel-shaped crater caused by an explosion with a typical slope made of released rocks in the Yamal-Nenets Autonomous District (YaNAO) in the southwest part of Yamal Peninsula in the area of the Mordy-Yakha River. The crater is situated in ice-enriched permafrost near a small lake, however, initially it was filled with water in its lower part only (Fig. 1). It had dimensions of 30 m in diameter and about 40 m in depth. A number of theories have been put forward to explain the crater origin including a meteorite impact and underground storage facility failure. A working group involving representatives from Russian Academy of Sciences institutes and other scientific institutions was established to gather information for analyzing the reasons of the craters' formation. Three expeditions have collected unique materials including water and soil samples from the crater, photo and video recording of the crater. The first expedition has documented that the content of methane significantly exceeds the background value. Subsequent measurements made by the second and third expeditions showed a zero content of methane both near and inside the crater (Bogoyavlensky et al., 2014). This means, that methane was one of components thrown out when crater formation (see Fig. 1).

The crater was filled by spring water quickly enough (Fig. 1), so it was impossible to take rock samples from the bottom. But some samples were taken in upper part of the crater from frozen deposits of the 3rd Marine terrace of Quaternary age (mQ_{III}^{2-3}). This geologic formation continues down to the depth 30–36 m or even 43 m (Structure and Properties of Permafrost Rocks in South Part of Bovanenkovo Gas-condensate Field, 2007) and represents considerable part of the crater geologic section, which is represented by Holocene organic matter-enriched brown silks (down to depth 1–1.5 m) and ice-enriched Late Quaternary (mQ_{III}^{2-3}) gray clays with ice content 25–50% vol. (depth 1,0–40,0 m). Permafrost rock sample was taken from inner side of the crater 1.5 m below day surface. The sample had mass about 2 kg and was represented by ice-enriched gray clay (mQ_{III}^{2-3}). According to (Streletskaya et al., 2006; Brushkov, 1998) this clay is represented by montmorillonite (about30%) with admix of illite and kaolinite (30%), silt (30%), sand (5%) and organic matter (5%). Natural total water content is in the range 40–50% mass. The clay is salted, salt content (Na-Cl type) is in the range 0.7–1.8% mass. High salinity provides high content of unfrozen water – up to 15–20% at −2.5 °C (*Structure and Properties of Permafrost Rocks in South Part of Bovanenkovo Gas-condensate Field*, 2007). The sample was packed in plastic bag, unfrozen and transported to Moscow from Yamal.

3. Experiment description

3.1. Sample preparation

The main purpose of the experiment was to find metastable hydrates response to temperature increase at subzero temperatures in salted frozen clay. Because the process of hydrate saturation of clay samples is a difficult task, and initial water content of the sample was lost, it was decided to dry a portion of the sample in oven and then saturate it by deionized water again. A piece of sample was put into oven with temperature +105 °C for 2 days. After that the sample was disintegrated in a mortar bowl to powder state. Then deionized water was added until semi-liquid consistency of the sample appeared. Water content was 43% mass that corresponded natural range of the parameter value (see above). Total volume of the prepared semi-liquid sample was about 300 ml.

3.2. Experimental equipment

The Gas Hydrate Autoclave System GHA 350 (PSL Systemtechnik GmbH, Figs. 2, 3) holding pressure up to 35 MPa with total working volume of 500 ml, equipped by three sapphire window, built-in magnetic stirrer, built-in double jacket for temperature control, pressure transducer for measuring pressure in test cell (measuring range 0–40 MPa, measuring accuracy 0.25% of full scale, measuring resolution 0,1 bar), temperature transducers for measuring temperature in test cell and bath (type PT100, measuring accuracy 0.1 °C, measuring resolution 0.01 °C) (Fig. 3) was used in the experiment.

Temperature in the autoclave was controlled by liquid circulating thermostat Huber ministat 230-cm^3 and a computer. Temperature and pressure inside the cell were measured by platinum resistance thermometer Pt100 (deviation ± 0.1 K) and pressure sensor P3276 (Tecsis GmbH, deviation ± 0.25% in the range 0–40 MPa).

Experimental cell with magnetic stirrer was chosen specially. Earlier experiments with hydrate formation in wet clays in static cells (see, for

Fig. 1. Ice crater in 2014 (left) and in 2015 (right).
(Photo by V.I. Bogoyavlensky.)

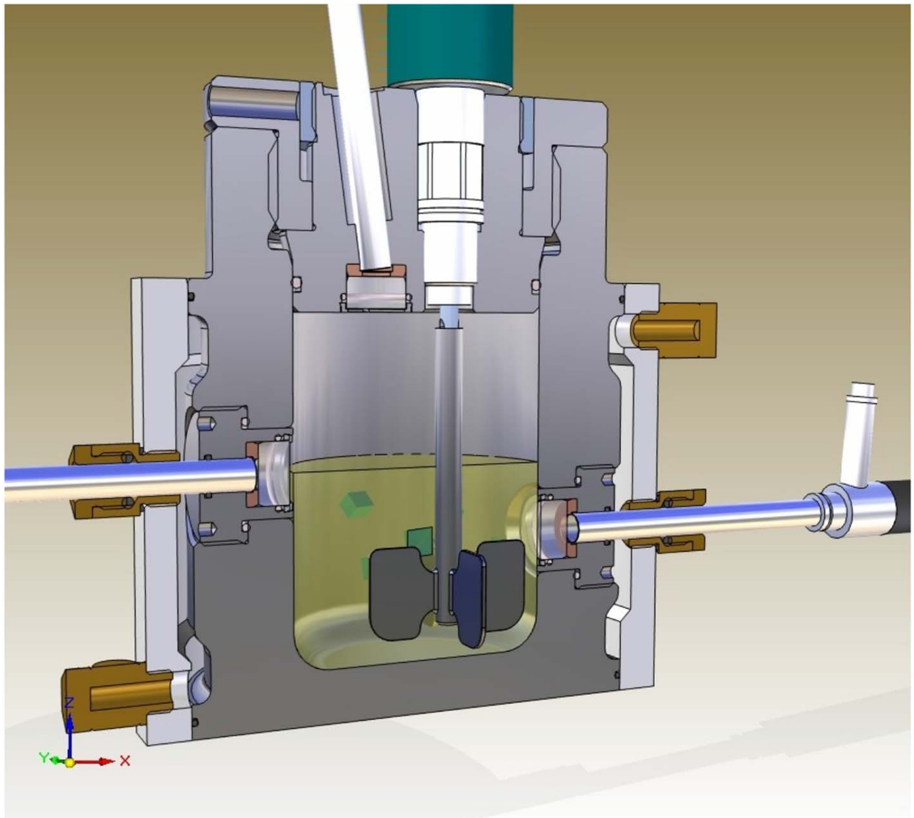

Fig. 2. Experimental cell (section).

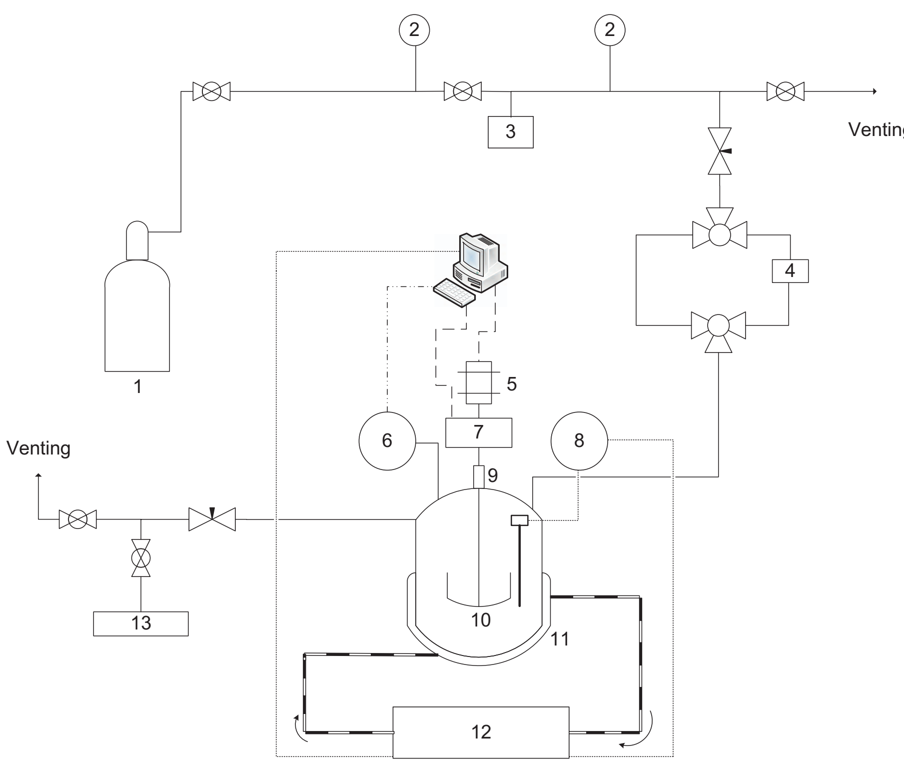

Fig. 3. Principal scheme of Gas Hydrate Autoclave System GHA 350.
1 – Gas cylinder; 2 – Pressure gauges; 3 – Gas booster; 4 – Buffer volume; 5 – Electric motor; 6 – Pressure sensor; 7 – Torque sensor; 8 – Temperature sensor; 9 – Magnetic coupling; 10 – Blade stirrer; 11 – Jacket; 12 – Circulating thermostat; 13 – Vacuum pump.

example Yakushev, 1990) have shown, that methane does not penetrate inside the body of wet consolidated clay with water content more than 10%. It forms very thin transparent hydrate film only on clay body surface. Hydrate content is so low, that cannot be detected by pressure change and the film presence is detected only when hydrate decomposition (withening and bubbling of the sample surface). The purpose of the stirrer was to make mix of wet clay and forming hydrates. Hydrate formation provided the mix viscosity growth and stirrer rotation stop at temperature above 0 °C.

3.3. Experimental procedure

Prepared sample was loaded to the autoclave at room temperature (+22 °C) and atmospheric pressure. Then the cell was hermetically closed and vacuumed to minimize air content in gas phase. Pure methane (CH_4 99.99% mol) was used for hydrate formation. Methane was injected into the experimental cell until pressure reached 10.6 MPa to have enough reserve of gas phase for hydrate formation. Then magnetic stirrer inside the cell was switched on and began to rotate with the rate 12 rpm (rotation per minute). Temperature of the cell was reduced from +22 °C to +0.65 °C during 2.5 h. The pressure inside the cell decreased from 10.6 MPa to 8.95 MPa in the same time. Pressure decrease is attributed to methane cooling and partial hydrate formation. The rock-water-gas system was deeply in the hydrate-stability thermodynamic region, but the stirrer continued to rotate indicating low hydrate content. The stirrer rotation continued 16,5 h more until it stopped due to sample viscosity increase at pressure 8.93 MPa, which is attributed to hydrate cement content increase. After 0.5 h of staying at temperature +0.65 °C the cell was began to cool down to temperature −7 °C. Temperature decreasing continued 4.5 h. Pressure at the end was equal 8.89 MPa. After that, the cell was left for 1.5 h to check completion of hydrate formation inside (by pressure stabilization). No considerable pressure change was observed. To transit stable hydrates to metastable (frozen) hydrates pressure was dropped to 0.002 MPa (atmospheric pressure) at temperature −6.8 °C during 1 min and autoclave was closed again. Temperature inside decreased to −8.5 °C and then began to grow back until it reached −6.83 °C in 0.5 h due to heating from thermostated jacket. Pressure increased to 0.013 MPa. Pressure increase should be caused by partial decomposition of gas hydrates in the clay and their transition to metastable, self-preserved state. The system was staying at these conditions about 20 min, no considerable pressure/temperature changes were observed. So autoclave was opened and pressure was dropped to 0.002 MPa (atmospheric pressure) again. Then the autoclave was closed and pressure changes were registered for 20 min. Temperature inside was −6.79 °C. No pressure change has been detected. That meant completion of remaining hydrates self-preservation process and their stabilization (if any remained).

To check the reaction of self-preserved, relic hydrates in frozen mineralized clay to heat impact, temperature growth in the cell was established with the rate 1 °C per 5 h. Pressure registration inside the cell was permanent with time interval 2 s. Pressure changes have been registered until the system reached temperature +2 °C (sure complete ice melting and hydrate decomposition).

4. Results and discussion

Slow temperature rise inside the autoclave caused irregular pressure increase. In the beginning of outer heating, when temperature inside was still the same as initial before heating, no pressure changes registered (Fig. 4, AB range), but slow heating of the clay caused remarkable pressure increase at temperature −6.75 (Fig. 4, BC range). Pressure increased from 0.002 MPa up to 0.032 MPa during 18 min when temperature within the cell was stable (−6.75 °C). So temperature change equal to 0.04 °C caused considerable gas release from preliminary thermally stabilized clay. This can be caused only by remaining metastable hydrates decomposition on exposed clay surface within the

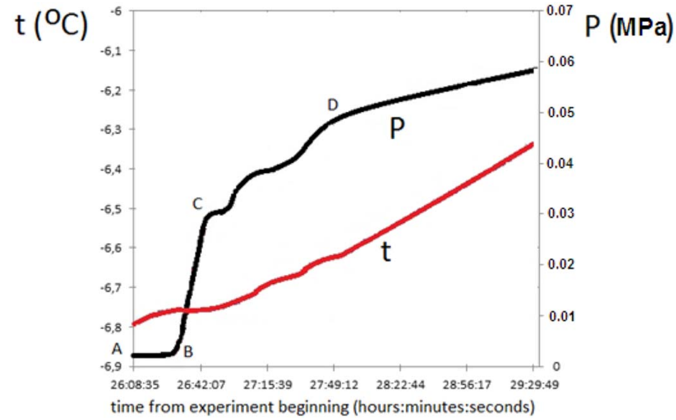

Fig. 4. Experimental curves of pressure (P) and temperature (t) changes inside the cell when slow heating of hydrate-containing sample.

autoclave. Further slow temperature elevation from −6.75 °C to −6.57 °C caused less intensive, but visible pressure growth from 0.032 MPa to 0.052 MPa (Fig. 4, CD range). This pressure growth can be caused by two combined reasons: remaining metastable hydrates decomposition in the clay volume (buried inside clay body when stirring) and some gas expansion with heating. During remaining time of the experiment pressure increased according temperature increase, no considerable deviation from constant growth gradient until 0 °C. In the temperature range −0.7–0 °C complete clay thawing took place and clay compaction resulted in some pressure reduction.

Clay represents a good mineral surface for gas hydrate growth (Istomin and Yakushev, 1992; Kuhs et al., 2014). But the possibility of hydrate formation in clays depends not only from clay permeability, but from clay water content too. Moreover, when clay water content is low (less than 6% mass for bentonite) clay is strong preventer of hydrate formation (Uchida et al., 2004). Water content growth causes more favorable conditions for hydrate formation and finally, when clay–-water system becomes liquid suspension clay can be promoter of hydrate formation (Uchida et al., 2004). So water content is very important for hydrate formation possibility in clays. In frozen clays considerable part of pore water is transformed into ice. Also a part of water is in unfrozen state. But if ice is favorable for hydrate preservation, unfrozen water easily destroys ice coating around hydrates, if its content is growing. Unfrozen water content growth in clays can be caused by heating and/or total mineralization growth (Principles of Geocryology, 2015).The rock sample used in the experiment had high bentonite content and was salted strong enough. It's unfrozen water content reached 15–20% at the temperature −2.5 °C (see above). So formed metastable hydrates were separated from pore unfrozen water by thin ice coating. The system comes to stabilization after depressurization in autoclave at constant temperature. Slow heating of the sample caused ice coating destruction and unfrozen water contact with metastable hydrates, that resulted in quick decomposition of them.

Permafrost soils often contain clay particles and are salted in different proportions. This means, that unfrozen water content also is very different in nature and its impact on metastable relic hydrates can appear at different temperatures depending on combination “mineral composition-water content-salinity-hydrate content-temperature”. Transmitting this regularity to natural conditions, one can expect gas shows and liberations from different permafrost rocks with relic hydrates at different temperatures (not only in the range −1–−2 °C as for sandy samples in experiments (Yakushev, 2009)). Moreover, even small changes (tenths or even hundreds of a degree) in temperature can cause considerable decomposition of relic hydrates in clay-enriched, salted permafrost rocks as it was observed in the experiment above. So even small climatic change and consequent heat wave penetration into permafrost section can cause considerable gas generation from shallow

Fig. 5. "Permafrost pockmarks" on Yamal thermokarst lake bottom.
(Photo of V.I. Bogoyavlenski from helicopter.)

relic hydrates.

Being decomposed hydrates should generate gas with pressure, equal to hydrate equilibrium at permafrost temperature, for example methane hydrate at temperature −6,75 °C is stable at pressure more than 2.1 MPa if deionized water (Istomin and Yakushev, 1992). Salt presence elevates stabilizing pressure. Due to high pressure, gas liberated from relic hydrates can migrate laterally and vertically trying to find exit from geologic section or place with good reservoir properties, where it could accumulate. At shallow depth this gas could create cavities of different scale with elevated pressure inside, especially in plastic clays with high content of unfrozen water. If cavity is large enough, it could generate breakthrough of its gas and water (if any mineralized water presents) to day surface (Fig. 1).

Gas breakthroughs from intrapermafrost relic hydrates to day surface should take place also when large thermokarst lake formation, because of rocks thawing below the lake bottom. In this case gas blowouts should remain funnels on the lake bottom, like pockmarks in seas (Judd and Hovland, 2007). And such "permafrost pockmarks" were observed in Yamal thermokarst lakes (Fig. 5), confirming version of gas generation inside permafrost, when section heating.

5. Conclusion

Intrapermafrost metastable hydrates can exist in salted clay sediments if ice coating formation around hydrates during self-preservation process is possible. But unlike in intrapermafrost sandy sediments metastable hydrates in salted clay sediments decompose at much lower temperatures (in the experiment conducted that was −6.75– −6.57 °C), than in sandy sediments. This means, that in real natural conditions even small elevation of temperature on permafrost day surface can cause considerable generation of gas (presumably methane) inside permafrost from relic hydrates (if any exist in the area) with short time. Moreover, permafrost rock layers with different mineral composition and water/ice content will generate gas from hydrates at different subzero temperatures depending on combination "mineral composition-water content-salinity-hydrate content-temperature". Gas generated from relic, metastable hydrates should migrate inside permafrost forming shallow gas cavities or exit to atmosphere. In thermokarst lakes it can form "permafrost pockmarks".

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